Softening of hard water (External treatment of Boiler Feed Water)

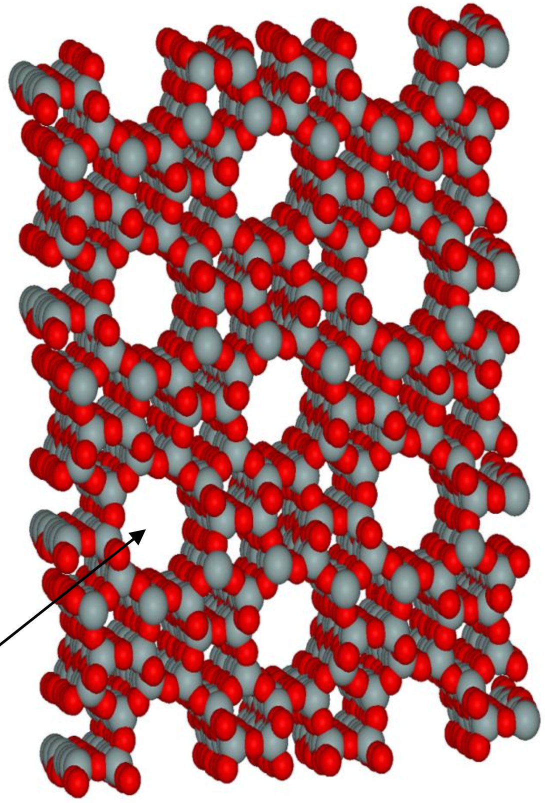
Zeolite (Permutit) method of Softening of water

Zeolite is a Hydrated Sodium Alumino Silicate, capable of exchanging its sodium ions with hardness producing cations in water.

The general chemical structure of zeolite is given below

$Na_2O.Al_2O_3.xSiO_2.yH_2O$

(x = 2-10 and y = 2-6)



Micro pores of Zeolite

Porous Structure of zeolite

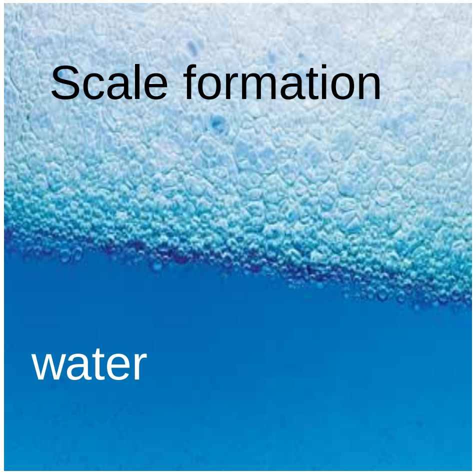
Process of softening by Zeolite method

Zeolite can be simply represented as Na_2Ze, where Ze represents insoluble radical which holds sodium ions loosely. When hard water is passed through Zeolite, Ca^{2+} and Mg^{2+} ions are retained by zeolite as CaZe and MgZe.

To remove temporary hardness

$Na_2Ze + \underbrace{Ca(HCO_3)_2}_{\text{Hardness}} \longrightarrow CaZe + 2NaHCO_3$

$Na_2Ze + Mg(HCO_3)_2 \longrightarrow MgZe + 2NaHCO_3$



To remove permanent hardness

$Na_2Ze + CaCl_2 \longrightarrow CaZe + 2NaCl$

$Na_2Ze + MgSO_4 \longrightarrow MgZe + Na_2SO_4$

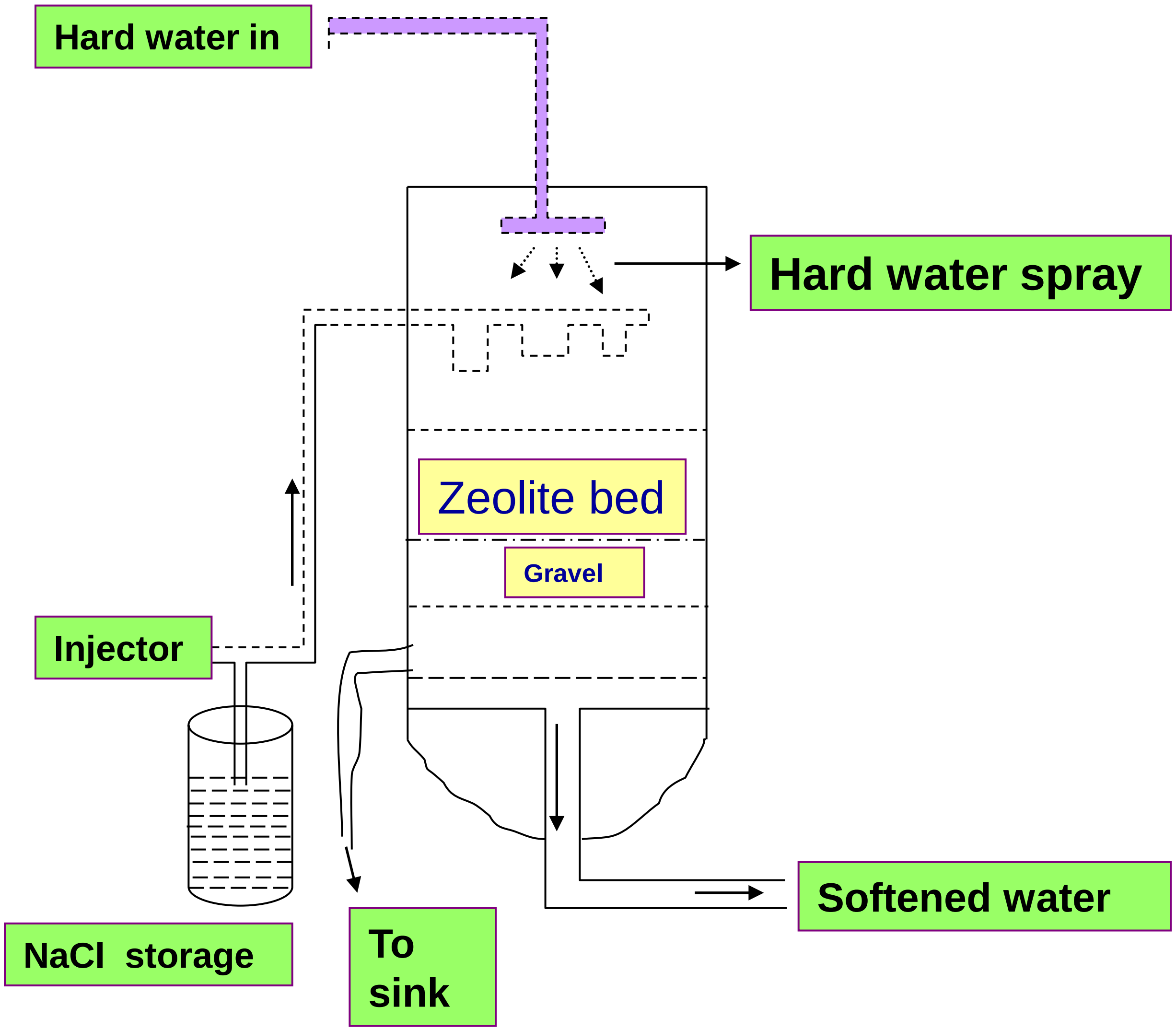
Regeneration of Zeolite Bed

After some time zeolite bed gets exhausted. Which is regenerated by using NaCl Solution (10% Brine Sol $NH_4Cl + NaOH \rightarrow NaCl + NH_4OH$)

$CaZe \text{ (or) } MgZe + 2NaCl \longrightarrow Na_2Ze + CaCl_2 \text{ or } (MgSO_4)$

Used Zeolite	10% brine solution	Regenerated Zeolite	Washings drained

Zeolite softener



Advantages / Merits of Zeolite process

1. It automatically adjust itself according to hardness of water.
2. Soft water of 10-15 ppm can be produced by this method
3. The equipment is cheap and occupies less space
4. It does not require more time and skill

Disadvantages / Limitations / Demerits of Zeolite process

1. If the water is turbid than output is reduced.
2. Treated water contains more sodium salts.
3. The process cannot be used with highly acidic water.

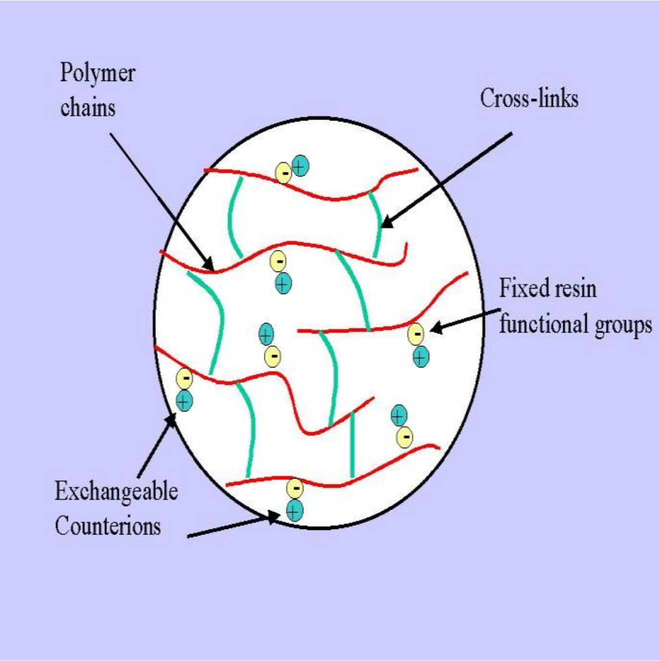
Quiz

- What is the formula of Zeolite?
- What is the another name of zeolite
- ____________ is used for regeneration of Zeolite Softner.
- Give the limitations of Zeolite Process.

FAQ

- **State the process for the removal of hardness of water? Discuss its merits over soda-lime process.**

Ion-Exchange resin



Ion exchange resin

Ion exchange resins are insoluble, cross linked, long chain polymers having functional groups responsible for the “ion-exchange” properties.

Types of Ion Exchange Resins: Two types

Cation Exchange Resins

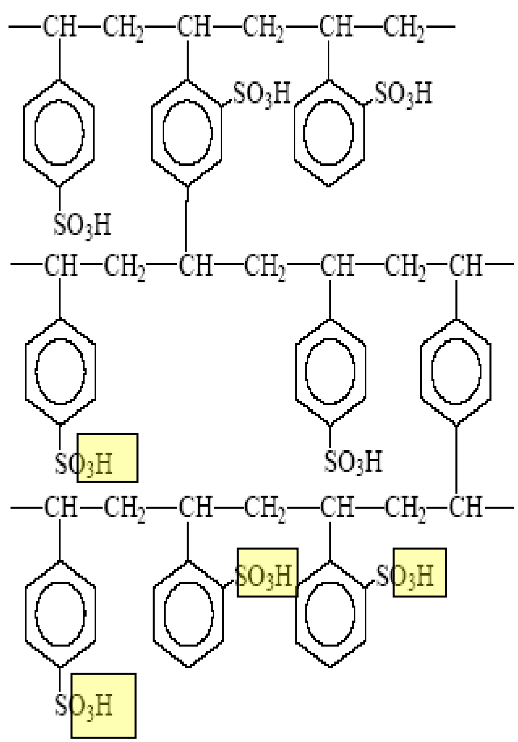
- These resins containing acidic functional groups (i.e. -COOH, $-SO_3H$ etc.) which are capable of exchanging their H^+ ions with Hardness producing cations.
- These are denoted by $R^- H^+$.
- **Example-** Zeocarb, Dowex-50 etc.

Anion Exchange Resins

- These resins containing basic functional groups (i.e. quaternary ammonium group) which on hydrolysis becomes capable of exchanging their OH^- ions with hardness producing anions.
- These are denoted by $R^+ OH^-$.
- **Example-** Dowex–3, Amberlite – 400 etc.

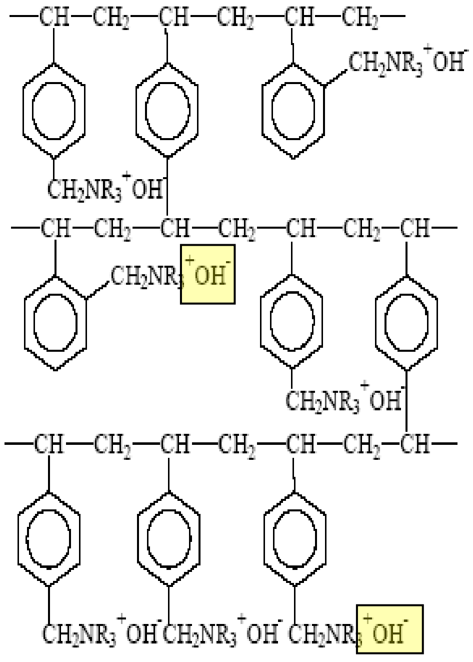
Structure of Cation and Anoin exchange resins

Cation exchange resin



A strongly acidic sulphonated polystyrene cation exchange resin

Anion exchange resin



A strongly basic quaternary ammonion anion exchange resin

R = CH_3

Water Softening

- The hard water is passed first through cation exchange column, which removes all the cations (like Ca^{2+}, Mg^{2+} etc.) from it and equivalent amount of H^+ ions are released from this column to water.

$$2R^-H^+ + Ca^{2+} \rightarrow R_2^-Ca^{2+} + 2H^+$$

$$2R^-H^+ + Mg^{2+} \rightarrow R_2^-Mg^{2+} + 2H^+$$

- Now hard water is passed through anion exchange column, where all the anions like Cl^-, SO_4^{2-} etc. are removed from water and equivalent amount of OH- ions are released from this column to water.

$$R^+OH^- + Cl^- \rightarrow R^+Cl^- + OH^-$$

$$2R^+OH^- + SO_4^{2-} \rightarrow R_2^-SO_4^{2-} + 2OH^-$$

- H^+ and OH^- ions (released from cation and anion exchange columns) get combined to produce water molecule.

$$H^+ + OH^- \rightarrow H_2O$$

Regeneration of ion exchange resins

cation exchange resin is treated with acid (dil HCl or dil H_2SO_4) and anion exchange resin is treated with a base (NaOH) solutions to regenerate these resins

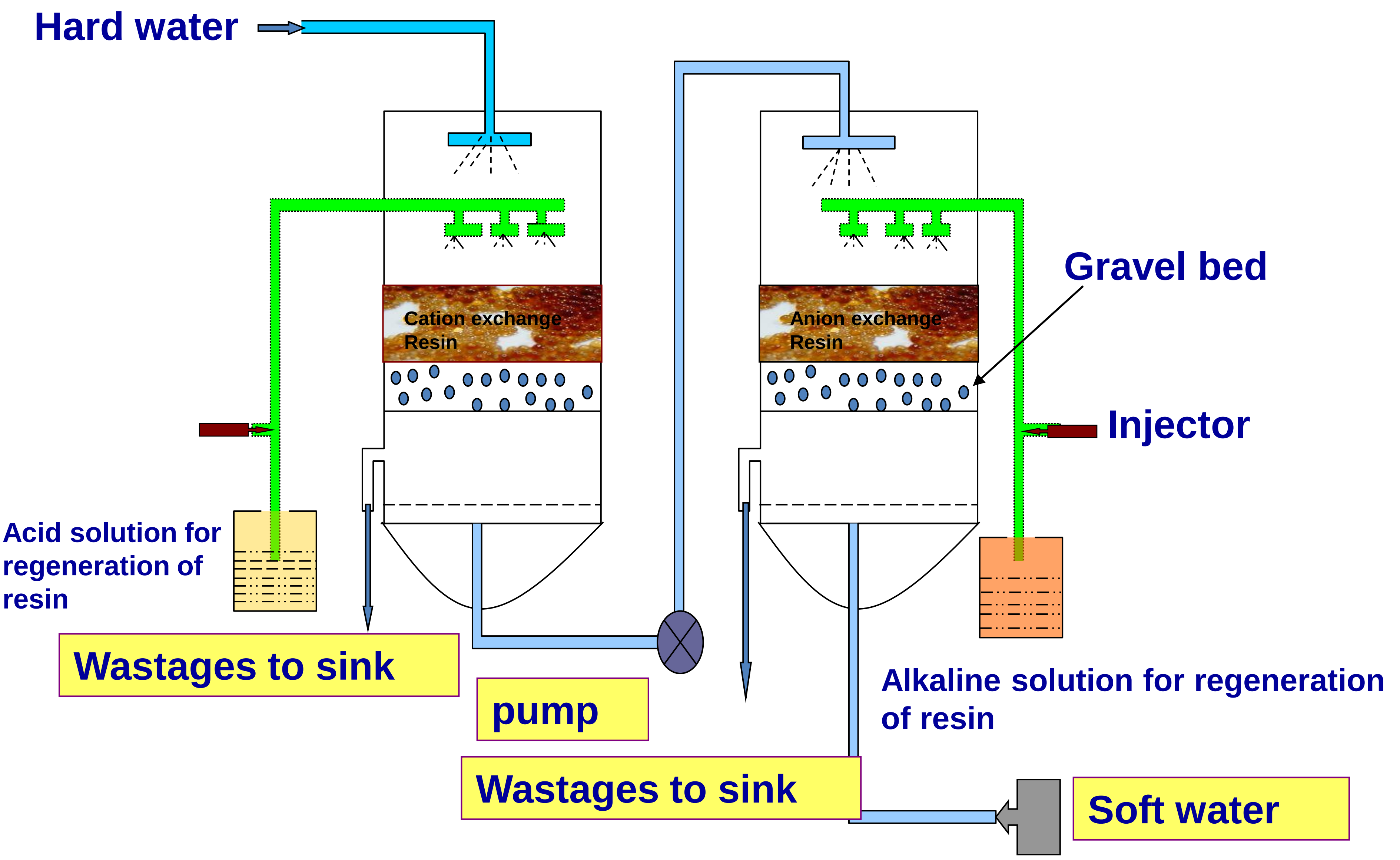
Regeneration of Cation exchange resin

$$R_2Ca^{2+} + 2H^+ \text{ (dil. HCl (or) } H_2SO_4) \longrightarrow 2\,RH^+ + Ca^{2+} \text{ (}CaCl_2\text{, washings)}$$

Regeneration of Anion exchange resin

$$R_2SO_4^{2-} + 2OH^- \text{ (dil. NaOH)} \longrightarrow 2\,ROH^- + SO_4^{2-} \text{ (}Na_2SO_4\text{, washings)}$$

Ion exchange purifier or softener



Advantages

1. **The process can be used to soften highly acidic or alkaline waters**
2. **It produces water of very low hardness of 1-2ppm. So the treated waters by this method can be used in high pressure boilers**
3. **It removes both types (cationic & anionic) of hardness impurities.**

Disadvantages

1. **The setup is costly and more expensive Chemicals are required.**
2. **It requires more time and space.**
3. **If turbidity is present output is reduced.**

Comparison of Zeolite Process and Ion Exchange process

Zeolite Process

- Advantages
  1. It automatically adjust itself according to hardness of water.
  2. Soft water of 10-15 ppm can be produced by this method
  3. The equipment is cheap and occupies less space
  4. It does not require more time and skill
- Disadvantages
  1. If the water is turbid than output is reduced.
  2. Treated water contains more sodium salts.
  3. The process cannot be used with highly acidic water.

Ion Exchange Process

- Advantages
  1. The process can be used to soften highly acidic or alkaline waters
  2. It produces water of very low hardness of 1-2ppm. So the treated waters by this method can be used in high pressure boilers
  3. It removes both types (cationic & anionic) of hardness impurities.
- Disadvantages
  1. The setup is costly and more expensive Chemicals are required.
  2. It requires more time and space.
  3. If turbidity is present output is reduced.

Quiz

- What are ion exchange resins? Give their types.
- Why Ion exchange process is called demineralization or deionization?
- Why Ion Exchange process is better than Zeolite process?
- ___________ is used for regeneration of cation exchange resin.
- ___________ is used for regeneration of anion exchange resin.
- What are the limitations of Ion Exchange process?

FAQ

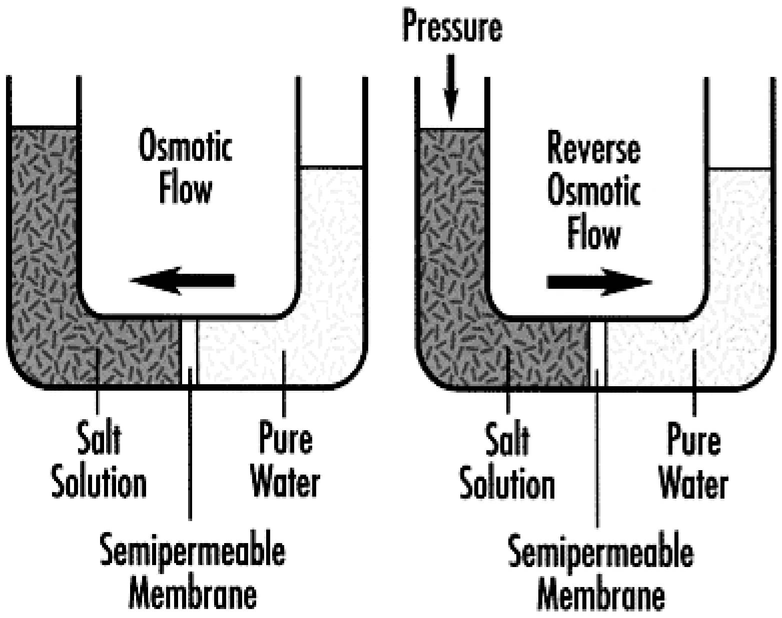
- **Discuss the Ion-Exchange or deionization or demineralization process for the treatment of hard water with its advantages and disadvantages.**

Reverse Osmosis

- When two solutions having different concentration are separated by a semi-permeable membrane, flow of solvent molecules from the lower concentration to higher concentration takes place, until the concentration becomes equal on both sides. This phenomenon is called **Osmosis**.

Or

- "**Osmosis** is the movement of pure water to solution."
- In **Reverse Osmosis** the above process of Osmosis is reversed by applying the external hydrological pressure (14.5 – 38.7 atm) on solution side (higher conc).

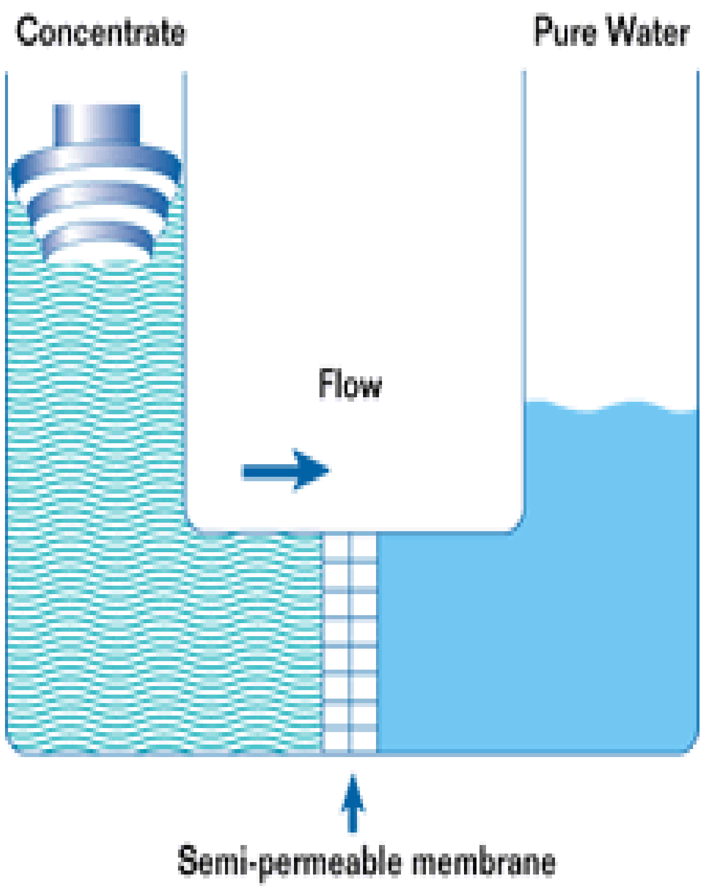


Advantage of Reverse Osmosis (RO) process

- It is simple and reliable process.
- Purification through RO removes all impurities of water.
- It operates comparatively at low temperature.
- The energy requirement is 30% lower than distillation process.
- The semi-permeable membrane has a lifetime of about 2years & it can be easily replaced within a few minutes.

Disadvantage of Reverse Osmosis (RO) process

A major problem with RO process is to find membrane strong enough to withstand the high pressure applied on it.



Applications

- Treatment of waste water,
- Desalination,
- In pharma industry
- In regeneration of minerals

Quiz

- What is reverse osmosis process?
- What are drawbacks of Reverse osmosis process?
- Why Reverse osmosis is the best process for water softening?

FAQ

- **What do you mean by Reverse osmosis? Explain its process and advantages?**

Lime soda process

It is a process in which Lime ($Ca(OH)_2$) and soda (Na_2CO_3) are added to the hard water to convert the soluble calcium and magnesium salts to insoluble compounds by a chemical reaction. The $CaCO_3$ and $Mg(OH)_2$ so precipitated are filtered off and removed easily.

It is further divided in to **two types**

1. **Cold lime soda process**
2. **Hot lime soda process**

Water Softening

- Lime removes temporary hardness, permanent hardness of (Mg^{2+}), CO_2, mineral acids, bicarbonates of Na and K, and $NaAlO_2$ or alums.
- Removal of temporary hardness of Ca^{2+} — $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$
- Removal of Temporary hardness of Mg^{2+} — $Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow Mg(OH)_2 + 2CaCO_3 + 2H_2O$
- Removal of Permanent hardness of Mg^{2+} — $MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + \boxed{CaCl_2}$

  $MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 + \boxed{CaSO_4}$
- Removal of CO_2 — $CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$
- Removal of acids — $2HCl + Ca(OH)_2 \rightarrow \boxed{CaCl_2} + 2H_2O$

  $H_2SO_4 + Ca(OH)_2 \rightarrow \boxed{CaSO_4 +} 2H_2O$
- Removal of bicarbonates of Na^+ and K^+ — $2NaHCO_3 + Ca(OH)_2 \rightarrow CaCO_3 + Na_2CO_3 + 2H_2O$

  $2KHCO_3 + Ca(OH)_2 \rightarrow CaCO_3 + K_2CO_3 + 2H_2O$
- Removal Fe^{+2} and Al^{+3} [These may be present in water as permanent hardness or may be added as coagulants]

  $FeSO_4 + Ca(OH)_2 \rightarrow \boxed{CaSO_4} + Fe(OH)_2$

  $Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow \boxed{3CaSO_4} + 2Al(OH)_3$
- Reaction with $NaAlO_2$ or Alum — $NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 + NaOH$

[Where, NaOH is equivalent to ½ $Ca(OH)_2$] — $2NaOH + Ca^{+2} \rightarrow Ca(OH)_2 + 2Na^+$

Amount of lime required for softening (L) = $\frac{74}{100}$ [Temporary hardness of Ca^{2+} + 2 x Temporary hardness of Mg^{2+} + permanent hardness of Mg^{2+} + CO_2 + ½ HCl + H_2SO_4 + ½ $NaHCO_3$ + ½ $KHCO_3$ + $FeSO_4$ + 3 x $Al_2(SO_4)_3$ – ½ $NaAlO_2$] in terms of $CaCO_3$ equivalents x $\frac{volume\ of\ water}{10^6}$ x $\frac{100}{\%\ purity\ of\ lime}$ kg

Water Softening

- Soda reacts with permanent hardness of Ca^{2+}

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

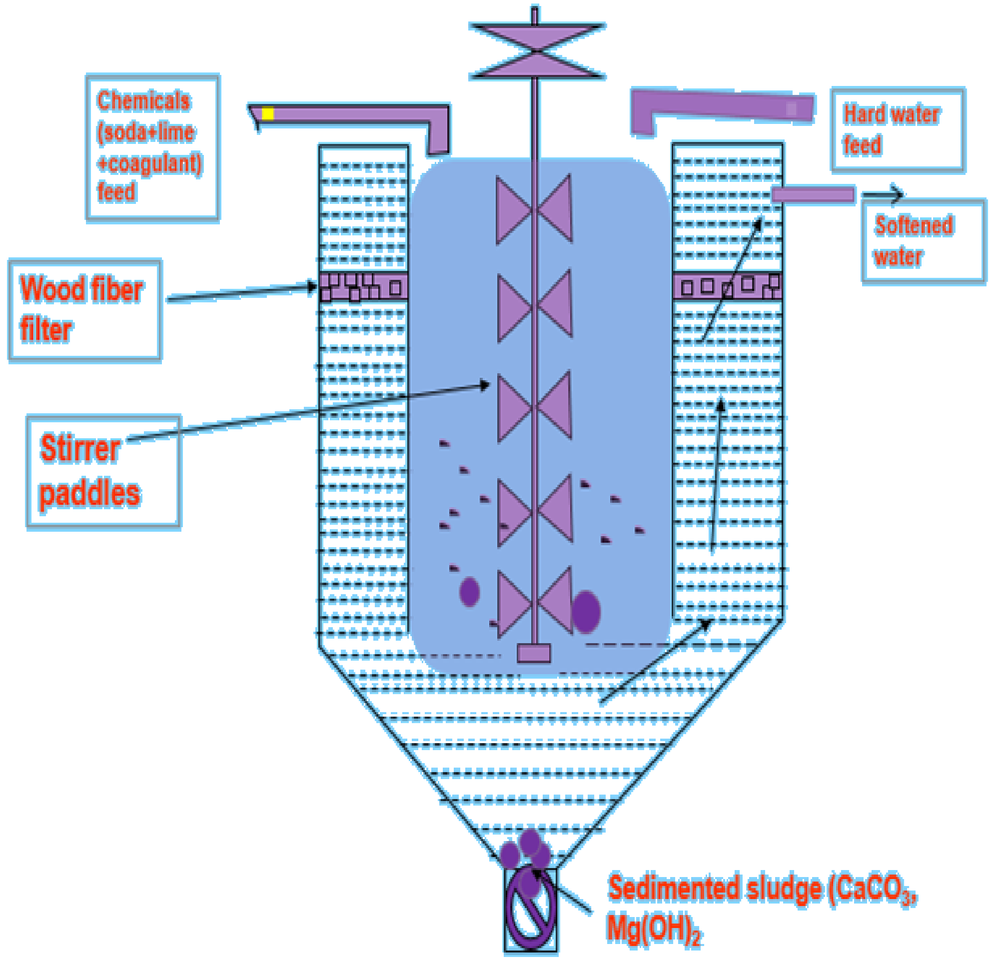
[It also reacts with $CaCl_2$ and $CaSO_4$ formed by removal of acid, Fe^{2+}, Al^{3+} to form $CaCO_3$.]

Amount of Soda required for softening (S) = $\frac{106}{100}$ [permanent hardness of Ca^{2+} + permanent hardness of Mg^{2+} + ½ HCl + H_2SO_4 + $FeSO_4$ + 3 x $Al_2(SO_4)_3$ – ½ $NaHCO_3$ – ½ $KHCO_3$] in terms of $CaCO_3$ equivalents x $\frac{volume\ of\ water}{10^6}$ x $\frac{100}{\%\ purity\ of\ soda}$ kg

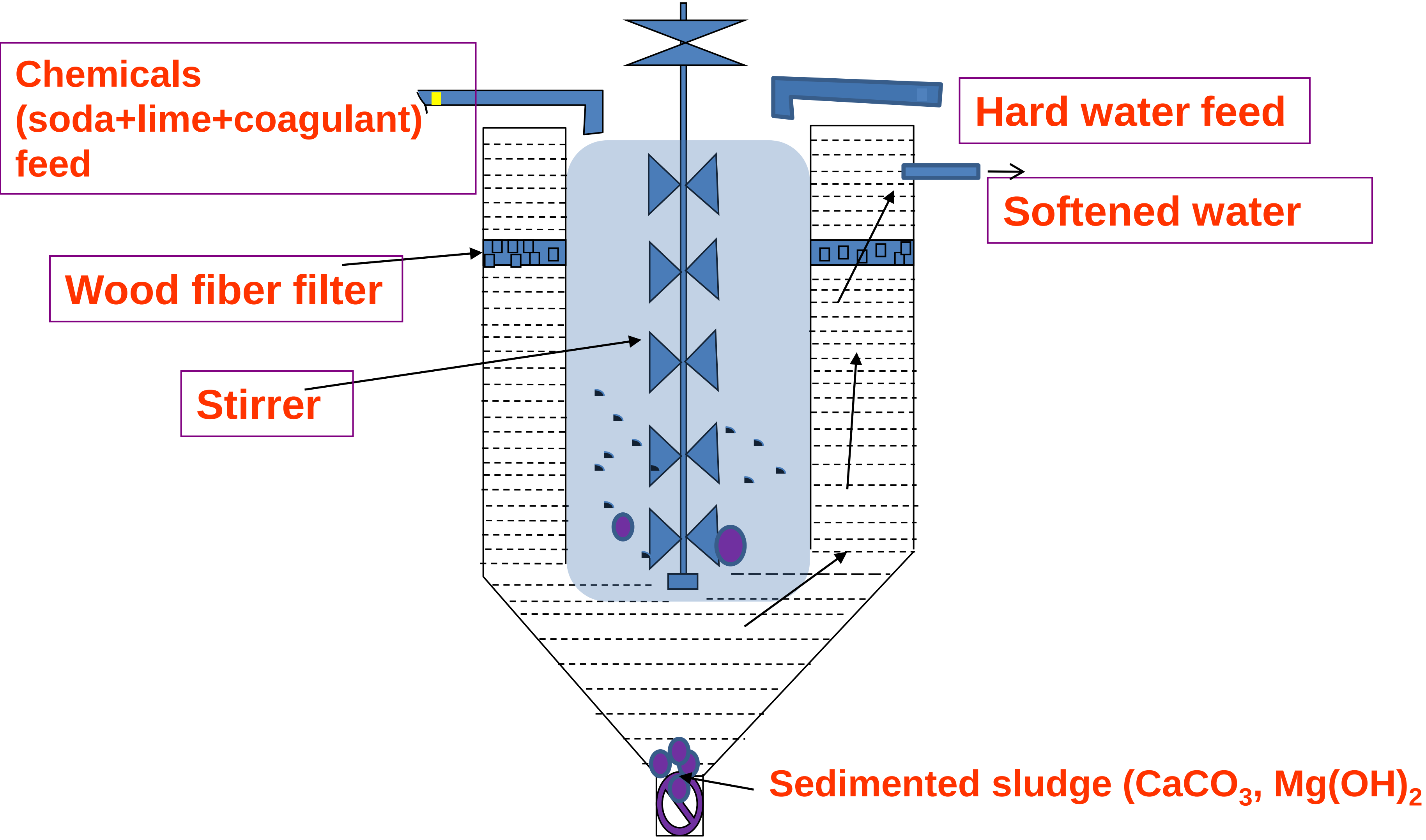
Types of Lime Soda Process

Cold Lime Soda Process

- Chemicals are added to hard water at room temperature.
- Raw water and calculated amount of chemicals are continuously added from the top with continuous stirring.
- Coagulants also added to fasten the precipitate formation.
- Precipitate Formed settles down at the bottom.



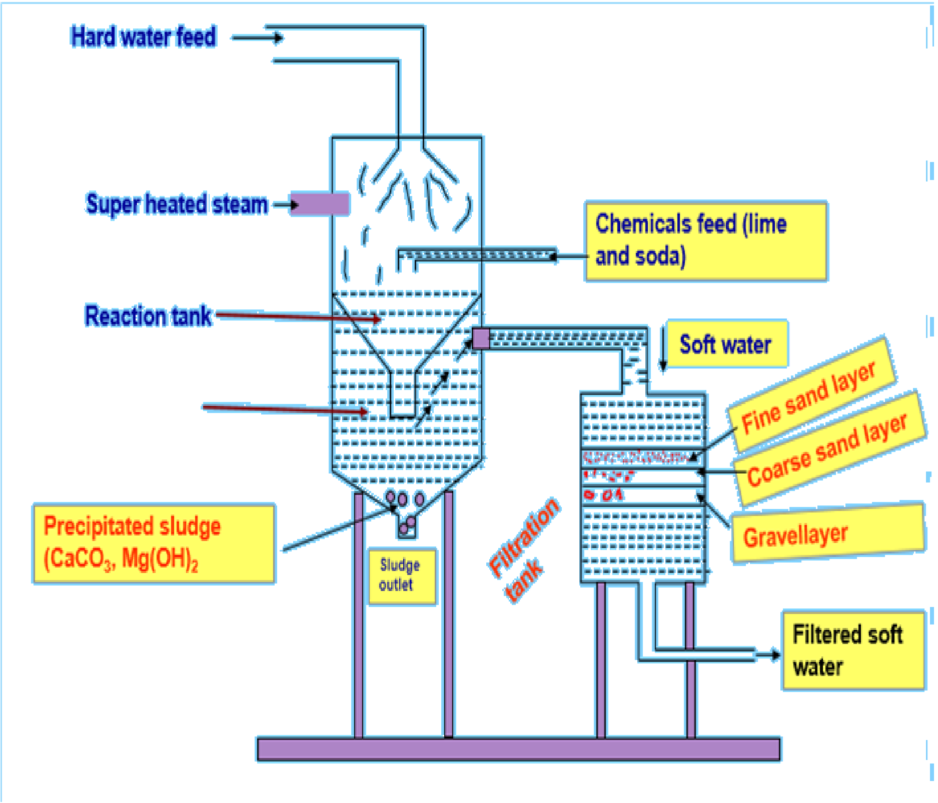
cold lime soda softener



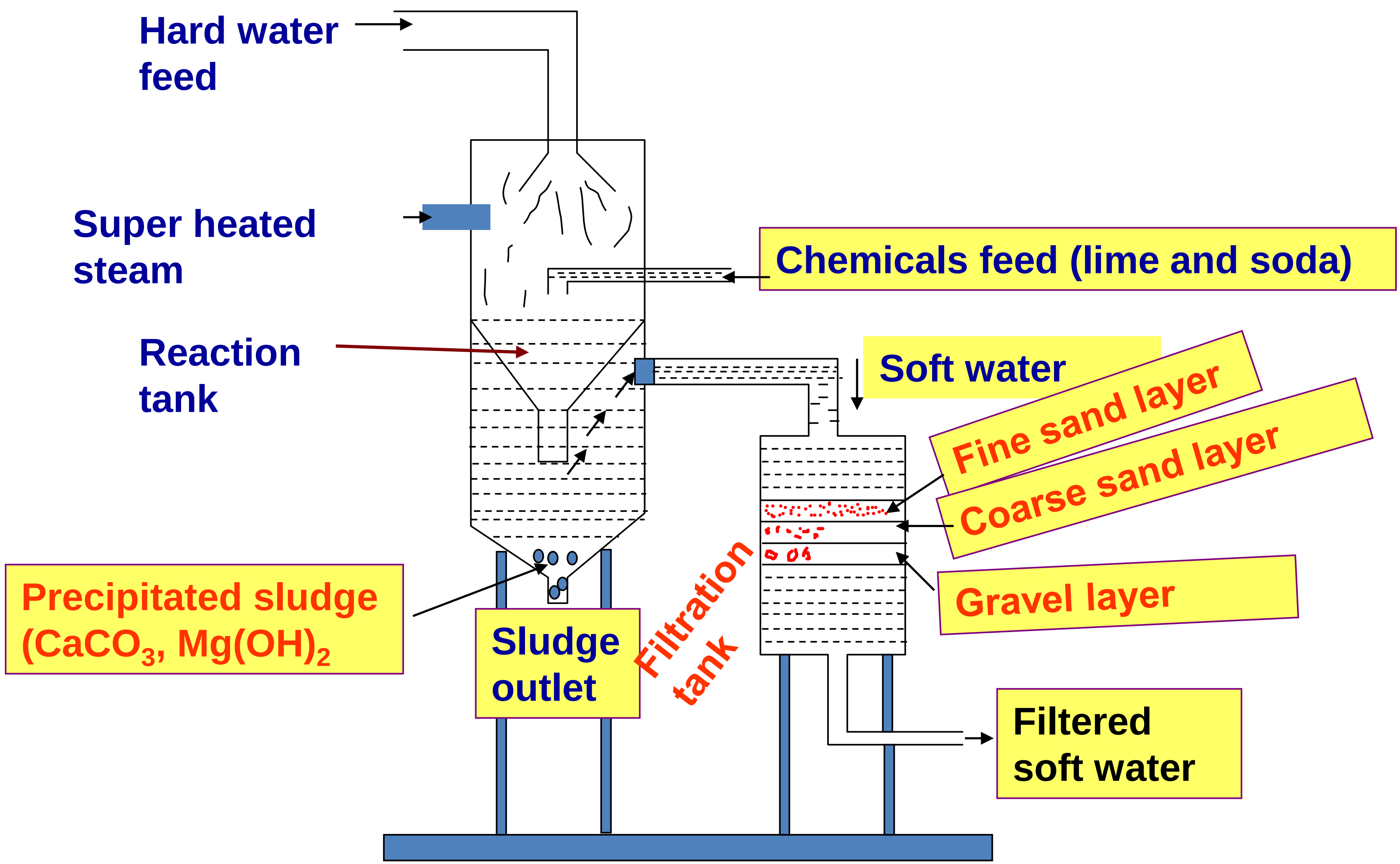
Types of Lime Soda Process

Hot Lime Soda Process

- Chemicals are added to hard water at 80^{o}C temperature.
- Raw water and calculated amount of chemicals are continuously added from the top.
- Since the reaction takes place at higher temperature, no or very less coagulant is required.
- Sludge Formed settles down at the bottom.



Hot Lime soda Process



Advantages of Lime soda process

- It is very economical compared to other methods
- Iron and manganese salts are also removed by this process
- It increases the pH of the softened water hence corrosion is minimized also pathogenic bacteria

Disadvantages of Lime soda process

- Disposal of large amount of sludge (insoluble precipitates) poses a problem
- This can remove hardness to the extent of 15ppm which is not good for boilers

Calculation of lime and soda required for the softening of hard water by the lime soda process

Hardness producing substance	Chemical reaction with lime and soda	Need
<u>Permanent Hardness</u>		
Ca Salts	$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaCl$	S
Mg salts	$MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaSO_4$ $CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + Na_2SO_4$	L + S
<u>Temp. Hardness</u>		
$Ca(HCO_3)_2$	$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$	L
$Mg(HCO_3)_2$	$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O$	2L
<u>Acids</u>		
HCl **H_2SO_4**	$2H^+ + Ca(OH)_2 \longrightarrow Ca^{2+} + 2H_2O$ $Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2Na^+$	L/2+S/2
HCO_3^-	$HCO_3^- + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + H_2O + CO_3^{2-}$	L/2 – S/2
$FeSO_4$	$Fe^{2+} + Ca(OH)_2 \longrightarrow Fe(OH)_2\downarrow + Ca^{2+}$ $Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2Na^+$	L+S
$NaAlO_2$	$NaAlO_2 + H_2O \longrightarrow Al(OH)_3\downarrow + NaOH$	L/2

Lime requirement for softening

$$= \frac{74}{100} \left[\begin{array}{l} T.H \text{ of } Ca^{2+} + 2 \times T.H \text{ of } Mg^{2+} + P.H \text{ of } Mg^{2+} + CO_2 + \\ \tfrac{1}{2} HCl + H_2SO_4 + \tfrac{1}{2} NaHCO_3 + \tfrac{1}{2} KHCO_3 + FeSO_4 + \\ 3 \times Al_2(SO_4)_3 - \tfrac{1}{2} NaAlO_2 \end{array} \right] \text{in terms of } CaCO3 \text{ equivalents} \times \frac{\text{vol. of water}}{10^6} \times \frac{100}{\%\text{ purity of lime}} \text{ kg}$$

T.H = temporary hardness

P.H = Permanent Hardness

Soda requirement for softening

$$= \frac{106}{100} \left[\begin{array}{l} P.H \text{ of } Ca^{2+} + P.H \text{ of } Mg^{2+} + \tfrac{1}{2} HCl + H_2SO_4 + \\ FeSO_4 + 3 \times Al_2(SO_4)_3 - \tfrac{1}{2} NaHCO_3 - \tfrac{1}{2} KHCO_3 \end{array} \right] \text{in terms of } CaCO3 \text{ equivalents} \times \frac{\text{vol. of water}}{10^6} \times \frac{100}{\%\text{ purity of soda}} \text{ kg}$$

Molecular weight of lime = 74

Molecular weight of soda = 106

Molecular weight of $CaCO_3$ = 100

Therefore, 100 parts by mass of $CaCO_3$ are equivalent to

(i) 74 parts by mass of $Ca(OH)_2$

(ii) 106 parts by mass of Na_2CO_3

Numerical based on Lime-soda Process

- Calculate the amount of lime and soda required for softening 15000 litres of water which analysed as follows: temporary hardness = 20ppm, permanent hardness of Ca = 15ppm, and permanent Magnesium hardness = 10ppm.

- Water sample was found to contains following salts:

$CaCl_2$ = 55.5 mg/l, SiO_2 = 20.0 ppm, $NaHCO_3$ = 12.6 mg/l, KCl = 250 mg/l, $MgSO_4$ = 48 mg/l, CO_2 = 2.2 ppm, Fe^{2+} = 2.0 ppm, $Al_2(SO_4)_3$ = 10.0 ppm and $Mg(HCO_3)_2$ = 43.8 mg/l Calculate the quantity of lime (85% pure) and soda (95% pure) for softening 50,000 litres of water.

- A water sample was found to contains the following salts in mg/l:

$CaSO_4$ = 20.4, $MgCl_2$ = 9.5 and HCl = 7.3 Calculate the quantity of lime (85% pure) and soda (80% pure) required for softening 80,000 litres of water. What would be the total cost of chemicals if lime and soda are Rs. 9 and Rs. 35 per Kg?

Numerical based on Lime-soda Process

- Calculate the quantity of lime and soda for softening 50,000 litres of water containing the following salts per litre – $Ca(HCO_3)_2$ = 9.2 mg; $Mg(HCO_3)_2$ = 7.9 mg; $CaSO_4$ = 15.3 mg; $MgSO_4$ = 15 mg; $MgCl_2$ = 3 mg and NaCl = 4.3 mg.

  Ans. L= 1.17 kg, S = 1.426 kg

- Calculate the amount of lime (74% pure) and soda (92% pure) required for softening 20,000 litres of water containing salts in mg/l- $MgCO_3$ = 84, $MgCO_3$ = 40, $MgCl_2$ = 95, $CaCl_2$ = 111, $Mg(NO_3)_2$ = 37, KCl = 30.

  Ans. L= 7.3 kg, S = 5.2 kg

Calculate the amount of lime (92% pure) and soda (98% pure) required for softening 30,000 litres of water containing salts - $Ca(HCO_3)_2$ = 40.5 ppm; $Mg(HCO_3)_2$ = 36.5 ppm; $CaSO_4$ = 34 ppm; $MgSO_4$ = 30 ppm; $CaCl_2$ = 27.75 ppm and NaCl = 10 ppm.

Ans. L= 2.413 kg, S = 2.433 kg

Quiz

- What are the formula of Lime and soda used in water softening process.
- Which process is better Hot or Cold Lime soda process?
- What are limitations of Lime soda process?
- Give the formula for calculating amount of Lime and Soda required.

FAQ

- **Discuss the hot Lime-Soda process for the treatment of hard water with its advantages over cold Lime-Soda process.**
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